

# SCIENCE FOR CERAMIC PRODUCTION

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## FORSTERITE CERAMICS BASED ON SOL-GEL POWDERS

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The sol-gel method is used to obtain highly dispersed sintering-active forsterite powders. These powders were used to produce sufficiently strong and dense ceramics without additives at a firing temperature of 1350°C, however, full sintering of forsterite is hampered by intense recrystallization.

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Forsterite ceramics find wide application in various sectors of engineering due to its high level of physicochemical properties. However, production of high-purity fine-crystalline dense ceramics based on forsterite, which makes maximum use its advantages, is a complicated problem. This is mainly related to the insufficiently wide interval of the sintered state (usually not more than 30°C) and the need for preliminary synthesis of forsterite at relatively high temperatures (over 1200°C).

For the purpose of decreasing the temperature of forsterite formation, there exist more complex methods for preparing a mixture of silicon and magnesium oxides than simple mechanical mixing of finely dispersed powders. These are usually chemical methods providing for highly homogeneous mixtures of initial components, in which distribution of components takes place virtually at the molecular level, which ensures complete synthesis under relatively low temperatures and a short exposure duration (USSR Inventor's Certificate No. 381644) [1].

Great interest in special methods for synthesis of powders is related not only to a high level of mixing of initial components, but also to the possibility for ceramics to inherit morphology and other characteristics of initial materials [1]. Chemical methods of powder preparation make it possible to control parameters determining powder properties. However, many of those methods are multistage, require complex equipment, and involve toxic reactants, which restricts their wide practical application.

Sol-gel technology is promising for production of highly disperse powders and has lately become widespread due to simplicity and availability of reactants and equipment used [2 – 4].

The use of this methods makes it possible to produce ultradisperse powders of a complex composition, lower the temperature of synthesis, and control the morphology and phase composition of material.

Research carried out at the Ceramics department of the D. I. Mendeleev Russian Chemical Engineering University [5 – 7] made it possible to implement an original variant of sol-gel technology for different compounds, including complex ones: sol of a water-soluble polymer acts as a medium, in which aqueous solutions of inorganic magnesium salts and colloid solution of the silica-bearing component are uniformly distributed. The research determined [7] the effect of the type of initial magnesium salts and the silica-bearing component on synthesis and properties of forsterite powders. Thus, using magnesium acetate significantly lowers the initial temperature of forsterite formation (active forsterite formation proceeds already at 600°C), compared to magnesium chloride, sulfate, citrate, and especially nitrate, whereas the amorphous form of silica (silica filler) is preferable to the crystalline form as the silica-bearing component. However, specific techniques for producing ceramics based on active forsterite powder are not yet developed.

The purpose of our study was the development of technology for dense and strong ceramics based on active forsterite powder synthesized using the sol-gel method.

The initial components for producing forsterite powder were magnesium acetate crystal hydrate  $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and silica filler (highly dispersed amorphous silica) as the silica-bearing component. A saturated solution of the initial component was mixed allowing for possible calcination loss to produce forsterite of a stoichiometric composition.

For better structuring, gel was aged for 1 day at room temperature and then dried, and porous spongy xerogel was obtained. Based on the data in [1] indicating that forsterite formation from xerogel proceeds at a temperature above

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700°C and ends at 1200°C, heat treatment of xerogel was carried out within a temperature range of 600 – 1200°C with an interval of 200°C. Xerogels were heated at a rate of 300 K/h with a 2-h exposure at the final temperature. The processes occurring in firing of xerogels and characteristics of these powders have been described in detail [7]. As the heat-treatment temperature grows from 600 to 1200°C, the amount of forsterite and the size of its crystals grows (up to 4  $\mu\text{m}$ ), and high activity of forsterite leads to its sintering with formation of intercrystal pores of size up to 2  $\mu\text{m}$ . For further studies we used forsterite powders obtained at temperatures of 600, 800, and 1000°C.

To increase the surface energy of the product of heat treatment of xerogel, it was disaggregated in a planetary mill for 5 min.

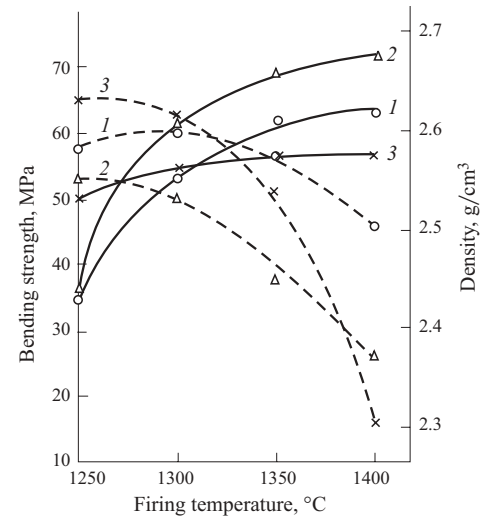
A temporary technological binder for molding samples was 5% aqueous solution of polyvinyl alcohol used in an amount of 20%. The PVA solution was added to the powder and then sifted via a nylon sieve.

Samples of size 4 × 4 × 40 mm were produced by the method of bilateral two-stage molding in a steel mold under pressure of 100 MPa on a P-10 press machine. Next, the samples were dried in a thermal cabinet for 2 h at 100°C.

The sinterability of sol-gel forsterite powders was investigated in an interval of 1250 – 1400°C with a step of 50°C. The exposure at the final temperature was 2 h. The temperature was monitored using a platinum-platinum-rhodium thermocouple.

A general tendency was observed in glass powders regardless of their temperature of synthesis: the higher the sintering temperature, the greater their shrinkage, shrinkage values being in inverse proportion to the depth of powder calcination. This is primarily related to higher activity (specific surface area) of powders calcined under a lower temperature, second, to the fact that forsterite formation in them is not finished and continues during sintering and thus increases shrinkage, and third, to poorer moldability of powders (a low density of molded product) with high dispersion.

However, higher shrinkage does not mean better final condensing: it was found that powders calcined at 800°C sinter to higher density (starting with 1300°C) than powders synthesized at 600 and 1000°C (Fig. 1). It should be noted that water absorption of powders synthesized at 800°C is the lowest in the whole temperature range considered; however, it has a common type of dependence on firing temperature: starting with 1350°C water absorption of samples made of all powders abruptly increases with increasing firing temperature. Since the density of samples in this case virtually does not change and even slightly grows, this phenomenon is attributed to increasing open porosity with a simultaneous decrease in the quantity of sealed pores. In other words, starting with 1350°C ceramics become overroasted, which is a usual phenomenon for forsterite that has a narrow sintered-state interval.



**Fig. 1.** Bending strength (dashed curves) and mean density (solid curves) of forsterite ceramics: 1, 2, and 3) powder synthesis temperature 600, 800, and 1000°C, respectively.

Overroasting of ceramics has a negative effect on its strength properties: starting with firing temperature of 1350°C an abrupt drop in bending strength is registered in all samples (Fig. 1). The decreased strength is related to recrystallization (growth of crystals and coalescence of pores) occurring with increasing temperature.

Thus, the majority of crystals in samples fired at 1250°C based on powder synthesized at 600°C have sizes 2 – 6  $\mu\text{m}$ . The intra- and intercrystal porosity totals 4% and the pore size is 1 – 4  $\mu\text{m}$ . As temperature increases to 1400°C, a substantial growth of crystals is observed (up to 8 – 15  $\mu\text{m}$ , occasional crystals reach 20 – 25  $\mu\text{m}$ ) and porosity increases to 7 – 10% (Table 1).

The structure of forsterite samples from powders synthesized at 800°C and fired at 1250°C is heterogeneous as well

**TABLE 1**

Forsterite ceramics	Temperature, °C		Forsterite crystal size, $\mu\text{m}$	Volume content, %	
	synthesis	firing		crystalline phases*	pores
1	600	1250	2 – 6	92 – 93 F, 3 – 4 P	4
		1400	8 – 15	86 – 87 F, 3 – 4 P	7 – 10
2	800	1250	8 – 10	88 – 89 F, 3 – 4 P	8
		1400	8 – 30	81 – 85 F, 3 – 4 P	12 – 15
3	1000	1250	10 – 20	88 – 89 F, 3 – 4 P	8
		1400	10 – 25	82 – 85 F, 3 – 4 P	15

\* F) forsterite, P) periclase.

(crystal size 8 – 10  $\mu\text{m}$ , intracrystalline porosity around 8%). The crystalline phase of magnesium oxide is distributed in material in the form of clusters of size from 10 to 40  $\mu\text{m}$ . The size of MgO crystals in these clusters reaches 2  $\mu\text{m}$ .

Forsterite synthesized at a temperature of 1000°C sinters more poorly than samples of other compositions, which is evidenced by the data on fire shrinkage, density, and water absorption (Fig. 1). An increase in firing temperature, although it does not lead to a perceptible growth of crystals, facilitates an increase in porosity and formation of slot-shaped pores up to 10  $\mu\text{m}$  long, which perceptibly decreases the strength of ceramics (from 65 MPa at 1250°C to 15 MPa at 1400°C).

Thus, despite the difficulties of sintering sol-gel forsterite powders and producing ceramics based on them, it is established that the densest ceramics can be produced using powder synthesized at a temperature of 800°C. This powder has a sufficient extent of forsterite formation, in contrast to powder calcined at 600°C, and a high specific surface area, in contrast to powder calcined at 1000°C.

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